

Method for Deriving Carboxymethyl Cellulose

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Abstract

Chemical conversions proceeding in solid substances under mechanical effects are of great practical importance. At solid-phase mechanochemical interaction of powder cellulose and rice husks with a carboxymethylation agent, i.e. sodium monochloroacetate, one obtained a product, the composition and properties of which are similar to commercial carboxymethyl cellulose. The given products were synthesized using laboratory microgrinder of a planetary type MA-1. Carboxymethyl cellulose obtained from powder cellulose is water-soluble product. Solubility of carboxymethyl cellulose synthesized from rice husks is about 80-95 %. Viscosity of 5 % aqueous solutions of the products from powder cellulose is about 2-5 mPa·s and viscosity of 10 % aqueous solutions of the products from rice husks is about 4-6 mPa·s. It corresponds to viscosity of 1 % solution of the commercial carboxymethyl cellulose. Carboxymethyl cellulose, obtained from powder cellulose and rice husks, represents a cheap product for petroleum, gas and building branches. Application of efficient and ecologically convenient solid-phase mechanochemical technology of carboxymethylation cellulose-containing products allows using accessible cellulose-containing scraps as raw material without their preliminary preparation and clearing. One can use carboxymethyl cellulose obtained by the solid-phase technology developed to control viscosity of water-based drilling fluids. Solubility and viscosity of these products depend on parameters of the processing and are compared to similar properties of commercial carboxymethyl cellulose.

Introduction

In recent years physical and chemical processes proceeding in solid substances under mechanical treatment have become the objects for experimental and theoretical investigations [1]. Chemical conversions of substances proceeding under the influence of mechanical forces are of great practical importance [2, 3]. They offer new challenges for the creation of new original methods intended to process various products and for the development of new technologies for the synthesis of materials with the desired properties [4]. The nature and mechanisms of mechanochemical phenomena are complicated, but nevertheless the results of basic and empirical research in the area of mechanochemistry find different applications.

In the whole world oil-producing industry feels an increasing need for diversification of natural biopolymers and polymer-based materials. In particular, cellulose esters are widely used. In this connection it is an urgent problem to search for new methods to

processing the raw materials and as a result to obtain water-soluble alkylated derivatives based on cellulose materials.

Cellulose – natural polysaccharide – is a substance existing in cell coats of plants. According to its distribution cellulose comes first among all organic substances. Being the base for plants, cellulose is a valuable raw material used to create useful products. This polymer is reproduced in nature and its resources can be inexhaustible. The presence of various sources of cellulose-containing materials (spoilt sheets, straw, rice husks, waste wood, sunflower waste etc.) makes promising their physico-chemical modification.

Rice husk – cellulose-containing vegetable product. It's represents a collateral product of production of rice. The rice husk consists of useful components and is suitable for use in various areas. As to chemical composition husk is a combined polymer system, containing lignin, pectin and hemicelluloses along with the base component - cellulose. Macromolecules of these components include hydroxyl groups, which can

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be subjected to carboxymethylation by alkylation agents.

Microstructure of rice husk has been studied by a microphotographic analysis. Microphoto of initial rice husk is given in Figure 1. The photo presents ordered cellulose structure of rice husk, this product contains about 40 % of cellulose.

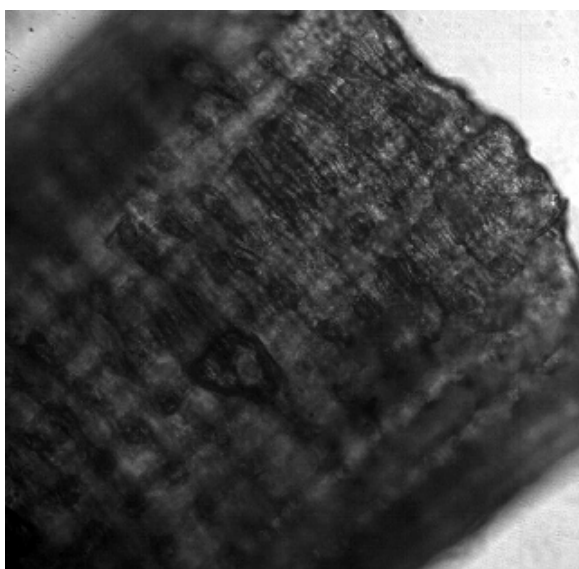


Fig. 1. Microstructure of rice husk.

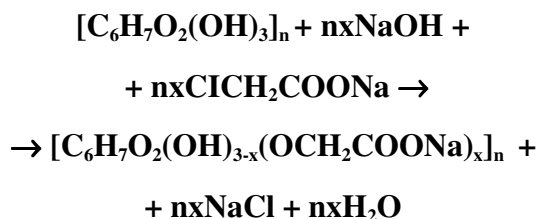
Now the problem of wasteless use of high molecular components of vegetative raw materials immediately in a vegetative fabric is urgent. The studies on the processing of vegetative substances without preliminary selection of any components are of great interest. In this connection rice husks in parallel with powder cellulose were used as the object under test.

The authors show availability of wasteless mechanochemical solid-phase technology of carboxymethylation cellulose-containing raw materials for deriving soluble products from powder cellulose and rice husks. At solid-phase mechanochemical interaction of powder cellulose and rice husks with a carboxymethylation agent, i.e. sodium monochloracetate, one obtained a product, the composition and properties of which are similar to commercial carboxymethyl cellulose.

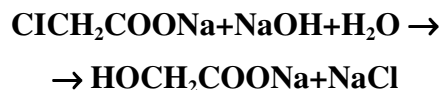
The researches of carboxymethylated products show, that the properties of carboxymethyl cellulose prepared from these initial cellulose-containing materials are comparable with those of commercial carboxymethyl cellulose, widely used as washing fluid for drilling of petroleum and gas slits and also in chemical and building industries.

Synthesis of carboxymethyl cellulose

Carboxymethyl ether of cellulose is a simple ether of cellulose and glycol acid. It's derived as sodium salts by means of interaction of alkaline cellulose with monochloroacetic acid or its sodium salt:



Simultaneously with a main reaction of carboxymethylation the collateral reaction of sodium monochloroacetate hydrolysis proceeds up to the formation of sodium salts of glycol acid.



The technical product contains a fair quantity of impurities. The contents of substituted carboxyl groups and homogeneity of their distribution also render essential influence on the quality of the product and depend on the character of process proceeding [5].

In Russia and abroad autoclave methods have been developed for industrial production of carboxymethyl cellulose. The existing processes of carboxymethylation are based on processing of cellulose by a water solution of sodium hydroxide with consequent extraction and blending of the obtained alkaline cellulose with alkylation agent (monochloroacetic acid or its sodium salt). One conducts the process in autoclaves under the conditions of elevated temperature and pressure. The indicated methods have a number of disadvantages: low operating ratio of the alkylation agent (about 50 %), high water discharge on realization of the technology, large volumes of sodium hydroxide solutions, availability of ecological harmful alkaline drains.

Taking into account the disadvantages of autoclave synthesis it is interesting to consider a possibility of carboxymethylation in a solid phase. The realisation of the reaction of carboxymethylation in solid phase with mechanochemical treatment makes possible to use all components of initial raw materials. Besides it allows to increase cellulose reactivity in the reaction of alkylation and to obtain a product with rather high contents of carboxymethyl groups. Mechanochemi-

cal technology is more economic and ecological pure. It allows to obtain a product as loose powder convenient for preparation of drilling solutions and dry mixtures, whereas some kinds of commercial carboxymethyl cellulose represent cotton-like product, which crushing represents an independent technical problem.

The solid-phase mechanochemical technology allows one to receive carboxymethyl cellulose with the contents of main substance not less than 40 %. Such product is quite suitable for use in drilling fluids. The clearing of the product from impurities is not made, since the requests to cleanness of carboxymethyl cellulose for drilling sites are much lower, than to this product for other industries (food, medical etc.). It allows using accessible cellulose-containing scraps as raw material without their preliminary preparation and clearing.

Experimental

Laboratory microactivator of a planetary type MA-1 (diameter of grinding balls is 8 mm, acceleration of the balls - 200 g) was used for mechanochemical synthesis of carboxymethyl cellulose.

Powder cellulose and rice husks were studied in a solid-phase reaction of carboxymethylation.

For the reaction of carboxymethylation powder cellulose were mercerized in 20 % solution of sodium hydroxide (3 mole NaOH on 1 mole cellulose). Then a sample was dried up at room temperature and subjected to mechanical treatment in the laboratory microactivator of a planetary type MA-1. Then sodium monochloracetate was added to carry out carboxymethylation in mechanoactivator (3 mole of sodium monochloracetate on 1 mole cellulose).

Rice husks also were mercerized in 20 % solution of sodium hydroxide (0,5 g NaOH on 1 g initial rice husks). Then a sample was dried up and subjected to mechanical treatment in the microactivator. Then 1 g of sodium monochloracetate on 1 g of mercerized rice husks was added to carry out reaction of carboxymethylation in mechanoactivator.

Carboxymethyl cellulose prepared from cellulose represents a white loose powder soluble in water, product from rice husks – brown powder.

IR-spectra of the samples obtained at “Spicord M-80”, were made in KBr tablets in the field of 400–4000 cm^{-1} . At the IR-spectra of all samples one observes characteristic absorption bands in the field of 1610, 1420, 1380 cm^{-1} , stipulated by oscillations of

carboxymethyl groups as sodium salts.

Rheological researches of carboxymethyl cellulose aqueous solutions were carried out with vibration viscosimeter «Reokinetica» with tuning gauge. This viscosimeter ensures continuous registration of the changed viscosity.

To define solubility of carboxymethylated products one prepared 1 % aqueous solutions of the samples, then washed out them by settlings on a filter and dried up to a constant mass.

The optimum components ratio has been selected experimentally. Depending on the time of carboxymethylation products with various solubility and viscosity have been synthesized. Solutions of some samples contain up to 20 % of suspended sediments and are characterized by a higher viscosity as compared with other samples, which differ by high solubility in water and form transparent solutions.

Results and Discussion

Activation of initial cellulose-containing raw materials is an important operation for deriving simple ethers of cellulose. Cellulose – is a high-polymeric system, in which the essential role is played by its physical structure. It is fair also for rice husks, which contain cellulose, lignin, pectin and hemicelluloses.

Mercerization promotes more complete carboxymethylation and ensures rectangular distribution of carboxyl groups in cellulose ether. During interaction of cellulose-containing materials with sodium hydroxide loosening of permolecular structure of vegetative substance happens. This effect facilitates a course of consequent reaction on hydroxyl groups of cellulose components.

The properties of carboxymethyl cellulose from mercerized cellulose and rice husks, synthesized using mechanochemical processing are indicated in Table 1 and Table 2. In the course of the experiment time of mechanical treatment of mercerized cellulose-containing products t_1 and time of mechanical treatment of activated cellulose and husks with sodium monochloracetate t_2 was changed. Sample solubility in water S and viscosity $1/\eta$ of 5 and 10 % aqueous solutions were measured.

Carboxymethyl cellulose prepared from powder cellulose is a water-soluble product independent of process parameters. Optimum time of carboxymethylation is 5 minutes, under this condition one obtained product with viscosity of 5 % aqueous solution about 4.5 mPa·s. Prolonging time of carboxy-

Table 1

Properties of carboxymethyl cellulose from powder cellulose

№	t ₁ , min	t ₂ , min	S, %	η at 20 °C, mPa·s
				5 %
1	5	5	100	2.1
2	7	5	100	4.5
3	7	10	100	1.5
4	7	20	100	2.7

methylation one can observe decrease in viscosity because of macromolecules destruction and decrease in molecular weight of the polymer.

In case of rice husks, if the time of carboxymethylation is 5-7 minutes, one can observe sedimentation in the solutions and their viscosity is about 1.5-2.5 mPa·s. If the time of carboxymethylation is 10 minutes, viscosity of the product is higher in connection with the high contents of suspended sediments in the solution. Prolonging time of carboxymethylation to 15 minutes higher solubility of the ether is achieved and the transparent solution is obtained. There are no suspended sediments in the solution.

One can see from the tables, that the value of viscosity for solutions of the synthesized carboxymethyl cellulose nearly coincides with the similar parameters for commercial carboxymethyl cellulose. Viscosity of 1 % solution of the commercial carboxymethyl cellulose is about 5-6 mPa·s.

Because of intensive mechanical forces in the planetary activator the destruction degree of the products is rather high. On the one hand, the lower molecular weight of these products ensures their high solubility in water, on the other - the higher concentrations of the ether are required for reaching viscosity value nearly coinciding with similar parameters for 1 % solution of the commercial carboxymethyl cellulose.

The rheological characteristics of the 5 % aqueous solution of the synthesized carboxymethyl cellulose from powder cellulose at thermostating are given in Figure 2. The analysis of rheological characteristics of the solutions showed that the nature of viscosity change for synthesized carboxymethyl cellulose solutions completely corresponds to viscosity change of commercial carboxymethyl cellulose solutions at thermostating. At heating of a solution to 40°C the minor lowering in viscosity is observed, however at

Table 2

Properties of carboxymethyl cellulose from rice husks

№	t ₁ , min	t ₂ , min	S, %	η at 20 °C, mPa·s
				10 %
1	5	5	79.6	1.7
2	5	7	82.3	2.5
3	5	10	83.9	5.8
4	5	15	92.6	4.6

further temperature increase the viscosity is sharply reduced.

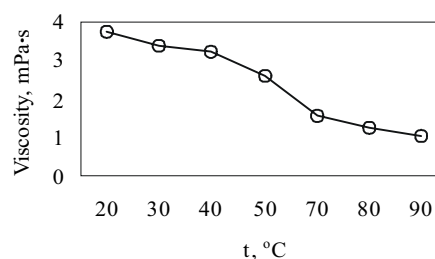


Fig. 2. The dependence of viscosity for 5 % aqueous solution of the carboxymethyl cellulose from powder cellulose on temperature.

Conclusion

The availability of efficient and ecologically convenient solid-phase mechanochemical technology of carboxymethylation cellulose-containing products is shown with reference to powder cellulose and rice husks. The conditions have been selected to derive carboxymethylated products with the desired properties.

The processing of rice husks is carried out by carboxymethylation of its high molecular components immediately in vegetative fabric.

Solubility and viscosity of synthesized products are compared to similar properties of commercial carboxymethyl cellulose.

The solid-phase mechanochemical technology allows using accessible cellulose-containing scraps as raw material without their preliminary preparation and clearing.

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Received 15 February 2001.